Analysis of NO formation during Earth entry using the Quasi Classical Trajectory Method

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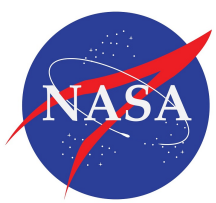

High Temperature Air Chemistry in Hypersonics

Goal :Understanding high-temperature, non-equilibrium chemistry for hypersonic flows

1. Prediction of the thermo-chemical non-equilibrium state
2. Atomic oxygen and nitrogen dictate heat shield oxidation and ablation
3. Improve thermal protection system design

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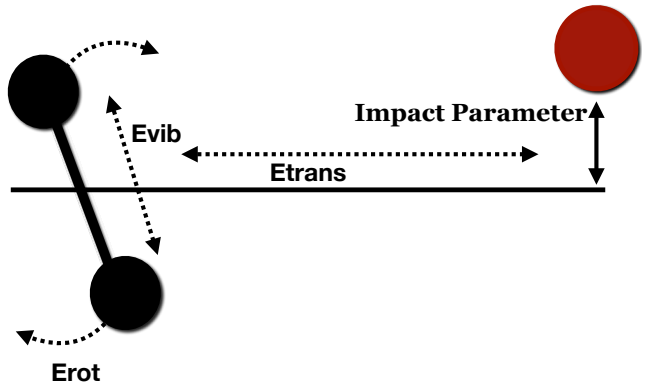
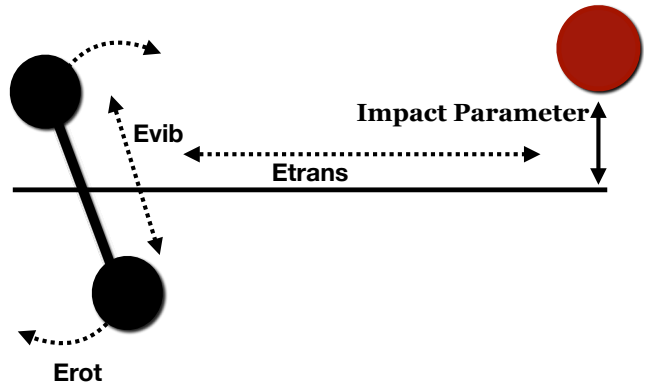
Current Focus:
What can we learn from QCT, besides obtaining rate constants, through N_2 + O interactions ?

Quasi Classical Trajectory Approach

1. Initialize reactants (quantized)
   - relative velocity of approach
   - impact parameter
   - Internal energy state
   - Randomize orientations of atoms
2. Integrate Hamilton's equations of motion
3. Analyze outcomes
4. Run lots of these calculations and analyze outcomes (statistically)



Quasi Classical Trajectory Approach



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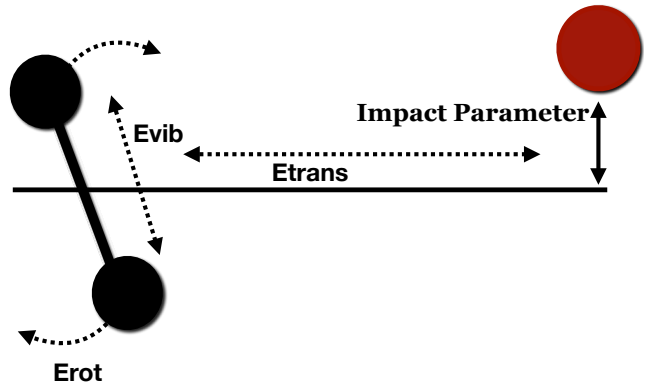
What do we need for the above? Forces on each atom.

- Potential energy surface (PES)

Quasi Classical Trajectory Approach



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For this work, REAQCT Code, developed at University of Minnesota has been used.

Potential Energy Surface for N_2+O

N_2+O interactions require two surfaces (A'' and A', ground triplet)

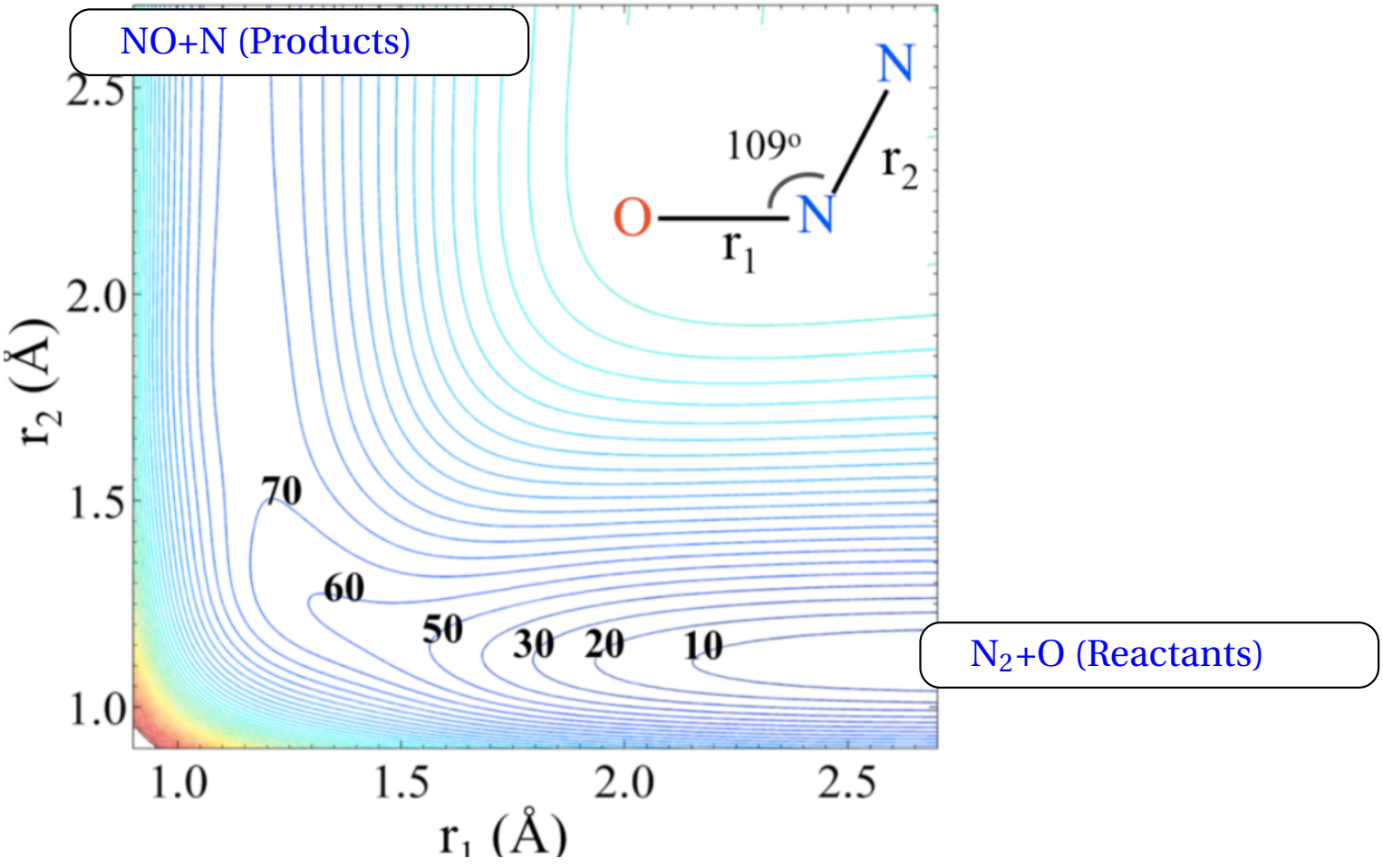

Figure: Contour plot for a possible NON geometry (Energies in kcal/mol)

Lin, W., Varga, Z., Song, G., Paukku, Y. and Truhlar, D.G., 2016. Global triplet potential energy surfaces for the N2 ($X\ ^1\sum$)+ O (3 P)→ NO ($X\ 2\pi$)+ N (4 S) reaction. The Journal of chemical physics, 144(2), p.024309

NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 1.0$ eV

$N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + N$

Dissociation energies: ϵ_d

$= 9.91$ eV (N_2) and 5.6 eV (NO)

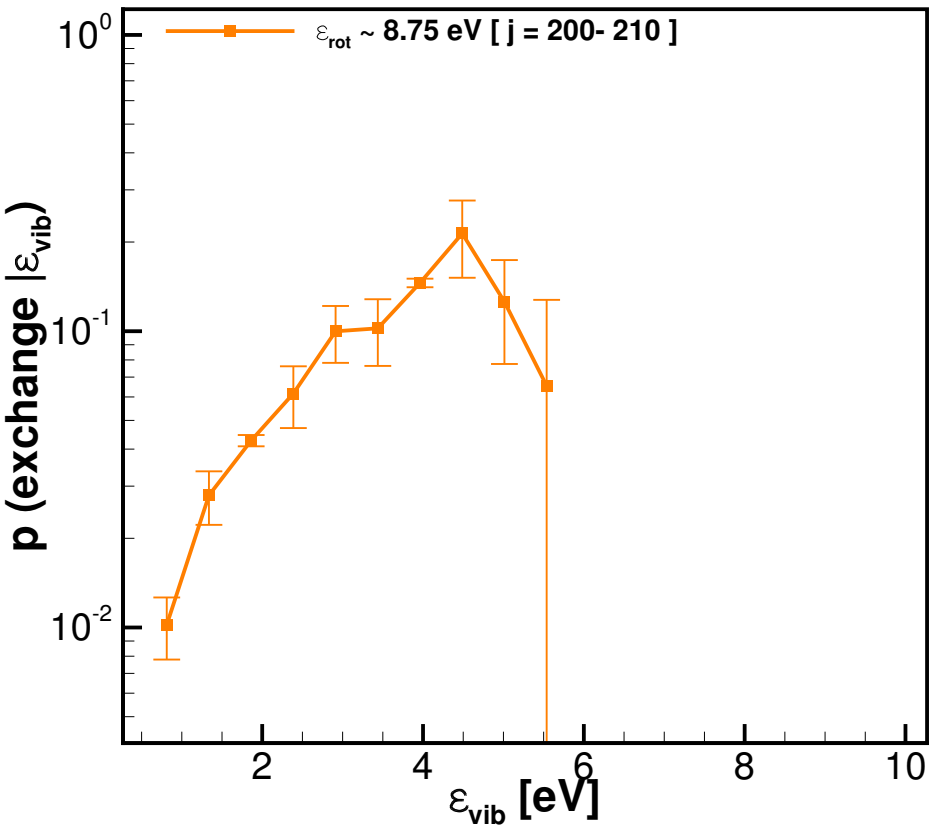

Figure: Exchange reaction probability vs. vibrational energy

Vibrational energy effect

- linear variation at lower energies
- nearly constant at higher energies

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Dissociation energies: ϵ_d

$= 9.91$ eV (N_2) and 6.62 eV (NO)

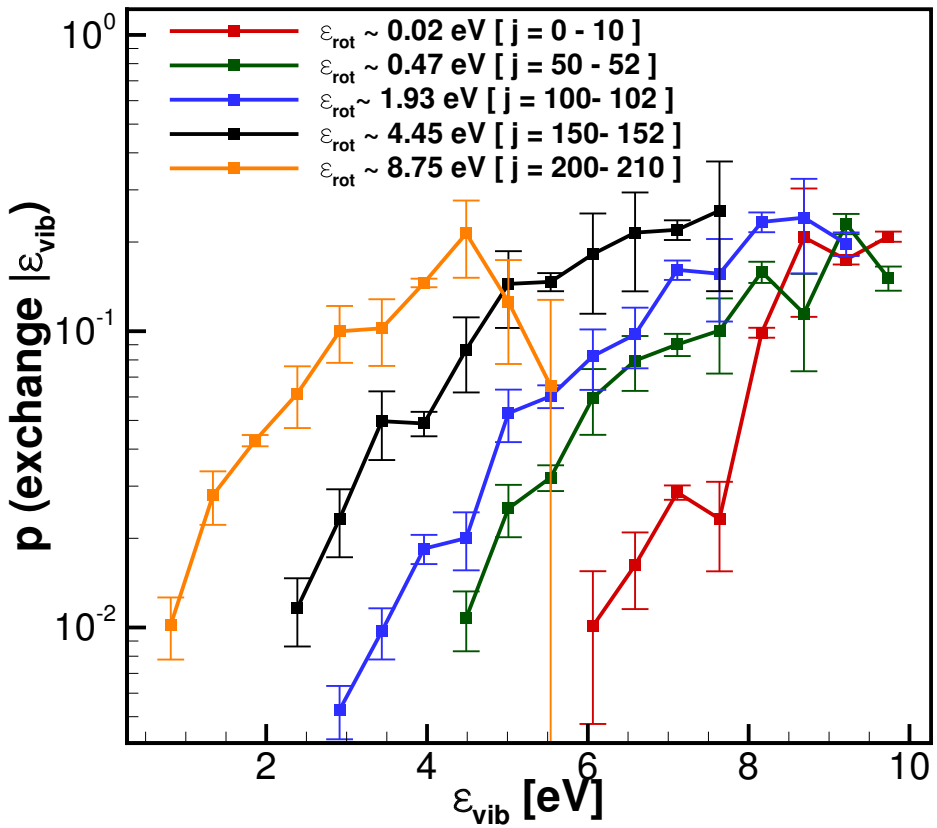


Figure: Exchange reaction probability vs. vibrational energy

Vibrational energy effect

- linear variation at lower energies
- nearly constant at higher energies

Rotational energy effect

- makes up for threshold energy

NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 3.0$ eV

$N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + N$

Dissociation energies: ϵ_d

$= 9.91$ eV (N_2) and 5.6 eV (NO)

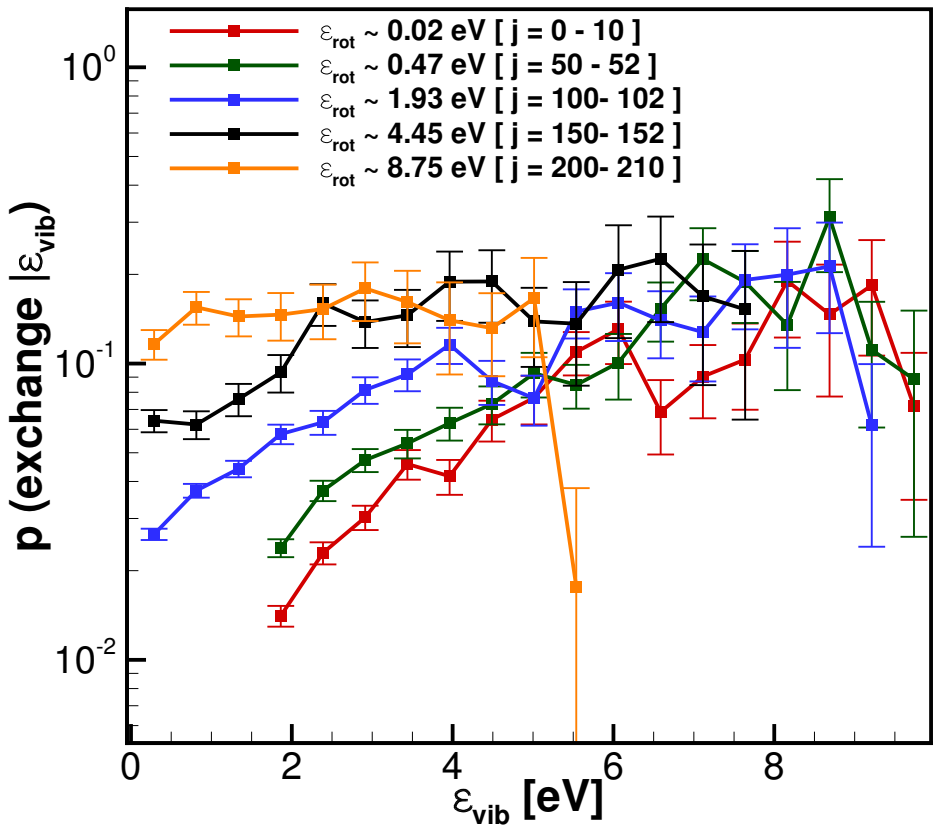


Figure: Exchange reaction probability vs. vibrational energy

Vibrational energy effect

- linear variation at lower energies
- nearly constant at higher energies

Rotational energy effect

- makes up for threshold energy

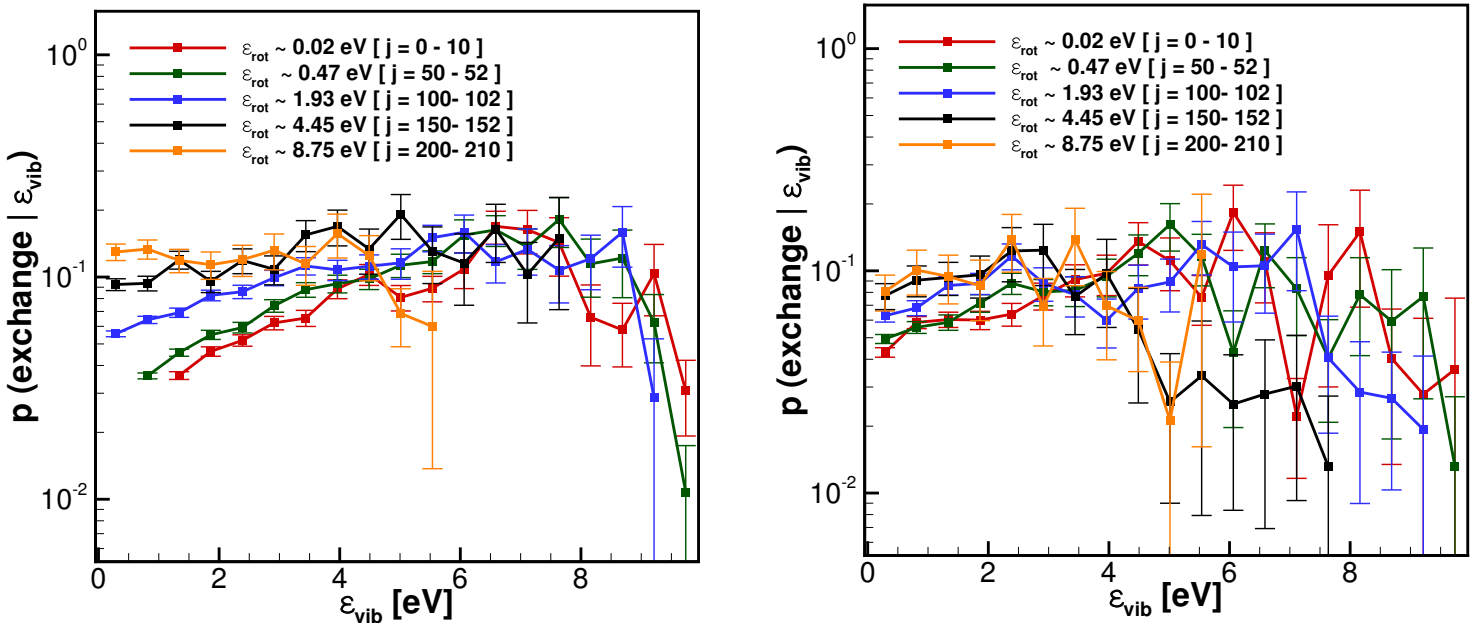
Translational energy effect

- Increase in ϵ_{trans} increases reaction probability

NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 5.0$ eV

Translational energy, $\epsilon_{trans} \approx 8.50$ eV

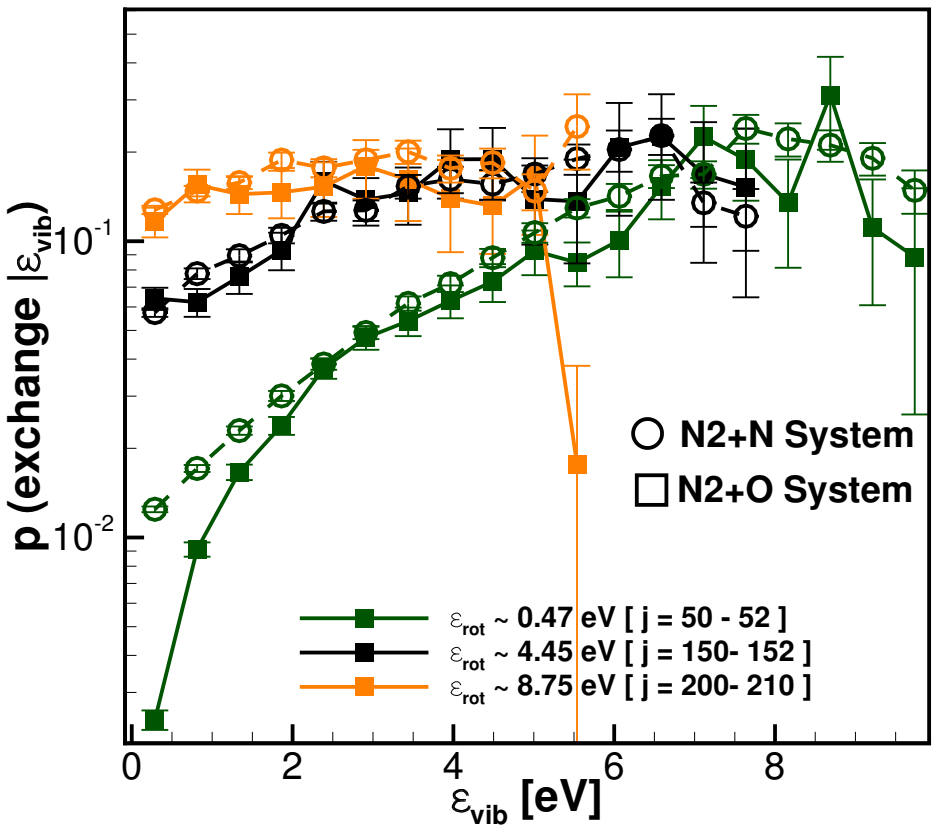


(a) (b)

Figure: Exchange reaction probability vs. vibrational energy, $N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + O$

Exchange Reaction Comparison: N_2 +O and N_2+N System

Translational energy, $\epsilon_{trans} \approx 3.00$ eV



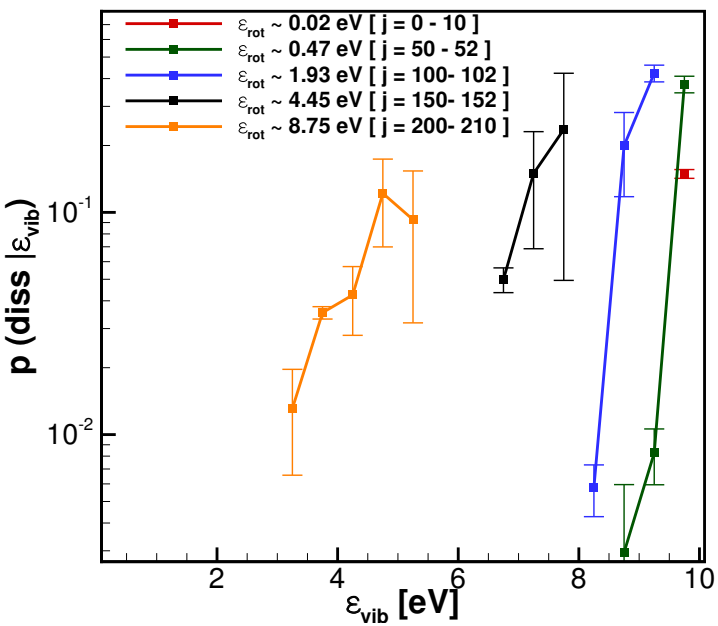
(a)

Figure: Exchange reaction probability vs. vibrational energy,

N_2 dissociation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 1.0$ eV

Translational energy, $\epsilon_{trans} \approx 3.0$ eV



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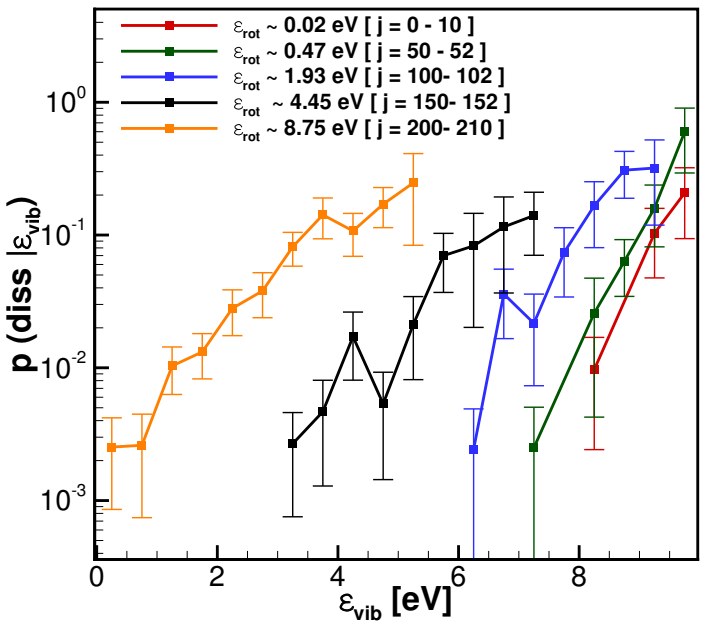

(b)

Figure: Dissociation reaction probability vs. vibrational energy, $N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow N + N + O$

N_2 dissociation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 5.0$ eV

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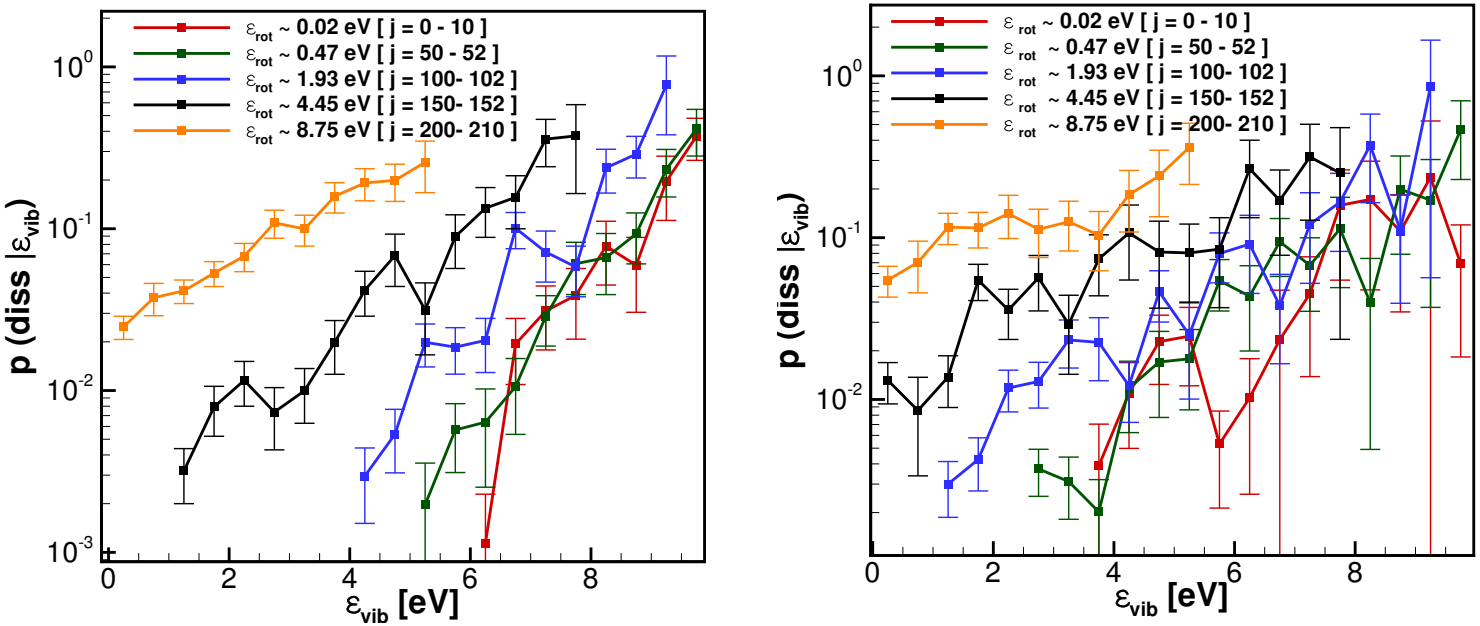
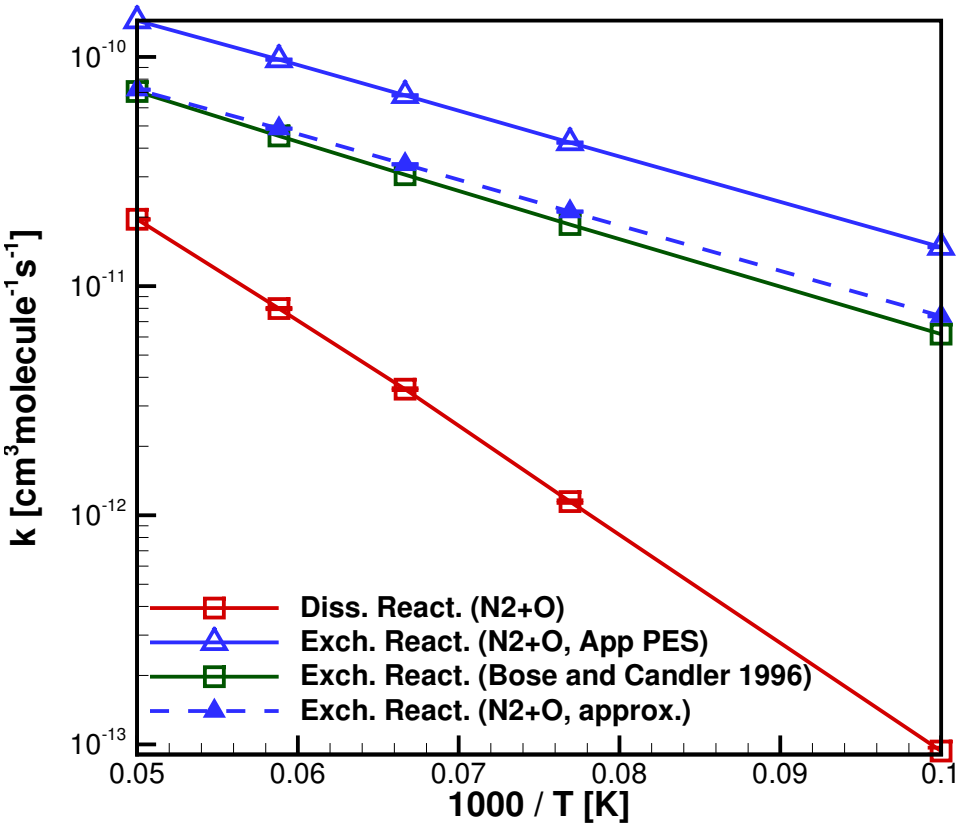


Figure: Dissociation reaction probability vs. vibrational energy, $N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow N + N + O$

Reaction Rate Constants for Various Temperatures



$$k = \frac{1}{3}\left[k(A'') + k(A')\right]$$
$$k(A')/k(A'') \approx \frac{1}{2},\ T > 12,000K$$
$$\Longrightarrow \text{k (approx.)} \approx k(A'')/2$$

Figure: Reaction Rate Constants

Conclusions

- Reaction cross-sections for exchange and dissociation reactions strongly depend on vibrational energy
- Reaction cross-reactions for dissociation has stronger dependence on vibrational energy
- On logarithmic scale, linear variation with vibrational energy for both reactions was shown
- The reaction cross-sections for interactions are not chaotic, in fact they have very simple trends. This is true for non-reactive interactions too (not shown in presentation)
- Simple trends are strong motivation to build simple models consistent with QCT information.

Thank you

Questions?